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TREATMENT

S. A. Hannah

Environmental Protection Agency
Cincinnati, Ohio

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S. A. Hannah
Environmental Protection Agency
National Environmental Research Center
Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio 45268

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S. A. Hannah*

Designers of wastewater treatment facilities in the near future will have to be capable of process design for nitrogen control.

Simply stated - in a great many areas we shall have to provide a nitrified effluent - in a few selected cases, nitrogen removal will be necessary. There is a great deal of capital and operating cost difference between these two considerations and careful process selection is a must.

The effluent requirements of the state will guide process selection but, in general, states are giving careful thought to standards on nitrogen. So far Illinois, California, Maryland, New York, Pennsylvania, Oklahoma, Georgia, Florida, Michigan, and the District of Columbia have established nitrogen control on selected watersheds. These cases are based on the role of nitrogen as a factor in eutrophication. There are use requirements that would necessitate nitrogen removal, such as water reuse applications, but these would be very specific case by case decisions. Most of the states listed are either directly or indirectly requesting in-plant nitrification, rather than nitrogen removal. The indirect requests come in the form of a very low ultimate BOD. The direct requests limit the concentration of ammonia in an effluent.

It appears, from laboratory and process experience to date, that 1-2 mg/l is about the lowest average concentration of nitrogen that can be expected from routine plant operation. This is because recycle streams can cause spikes of ammonia to appear in the effluent, and the vagaries of daily operation cannot be 100 percent controlled. From an engineering standpoint, if a 1 mg/l or less standard must be met, the design will be for 0 mg/l. It is hoped that improved monitoring and control equipment under development will result in greater efficiency and consistency of nitrogen removal.

*Presented by S. A. Hannah, Supervisory Research Chemist, at the Atlanta Design Seminar October 27-29, 1971.

Nitrification might also be provided in view of the more stringent effluent requirements being considered for disinfection. Chloramines are not as effective disinfectants as free chlorine.

Table I lists these various environmental considerations for nitrogen.

It is apparent that the major action on nitrogen control, in the near future, will concern the oxygen demand of ammonia nitrogen. Table II illustrates the reason for this. You can see that even if very efficient organic carbon removal from municipal wastewater is provided, by either conventional biological or chemical-physical processes, an effluent with over 100 mg/l of oxygen demand can be discharged.

Basically we can consider processes for control of nitrogen in two broad categories - biological and chemical-physical. Because of the importance of nitrogen, a number of studies on nitrogen removal processes have been supported. Table III lists the various approaches that have been evaluated. The first entry on the Table represents the ammonia stripping process as first investigated at the South Tahoe Advanced Waste Treatment Plant.

When wastewater is treated with lime to raise the pH, ammonium ion is converted to dissolved ammonia which may be stripped out by contacting the wastewater with large volumes of air in a stripping tower. Removals of 90 percent of ammonia nitrogen have been achieved in warm weather with 400 ft³ air/gallon of wastewater. Since ammonia is more soluble in cold water than in warm water, more air must be supplied as temperature drops to avoid loss of stripping efficiency. If the wet-bulb air temperature falls below 0°C, freezing may occur in the tower. Stripping is therefore not recommended for cold climates where year-round nitrogen removal is required. Neither is stripping recommended upwind of large bodies of water where rainout of ammonia into the water will undo all that has been accomplished. Tower designs are being improved in an attempt to minimize problems of calcium carbonate scale formation when lime saturated wastewater reacts with carbon dioxide in the air. The cost of ammonia stripping is

estimated at 2-4¢/1000 gal.

The use of natural ion-exchange materials such as clinoptilolite has shown favorable efficiencies for removal of ammonia from secondary effluents during large pilot plant demonstrations. Clarified water is passed through two ion exchange columns in series. When ammonia breaks through the second column, the first column is taken offstream for regeneration and a third column containing freshly regenerated clinoptilolite is added after the second column which now becomes the first in the series. Regeneration is accomplished by backwashing with limewater containing sodium chloride. The biggest factor to be resolved in this process is the processing of the concentrated brine solution, with a high ammonia content, that results from the regeneration of clinoptilolite.

Synthetic ion-exchange resins have been investigated for the removal of nitrate ions from secondary effluents. Limited success has been achieved because resins with a high selectivity have not been developed, regeneration of selective resins is usually inefficient; and as in the case of clinoptilolite, a concentrated, nitrogen-rich brine must be disposed of or processed for reuse as regenerant.

Almost all soluble nitrogen compounds in wastewater are in ionic form; and, therefore, theoretically 85-90 percent of these materials could be removed by demineralizing or de-salting processes such as reverse osmosis, electrodialysis, or distillation. None of these processes has a favorable selectivity for either ammonium or nitrate ion; and, therefore, it would be necessary to remove about 85-90 percent of all the salts in wastewater in order to remove 90 percent of the soluble nitrogen forms. Distillation is very unfavorable, since ammonia would be transferred to the distillate unless the feed is kept acidic; but even under these conditions, nitrous acid can distill over. All these processes produce a concentrated brine for disposal. These general salt removal processes are of interest only for wastewater that is to be reused, and are too expensive for consideration as treatment for wastewater to be discharged to surface waters.

Another approach which is being evaluated is breakpoint chlorination

for nitrogen removal. Breakpoint chlorination has been applied for many years for drinking water supplies. Recent studies of this approach as applied to secondary effluents have shown that essentially all the ammonia can be oxidized to nitrogen gas. Side products such as nitrate and nitrogen trichloride can be produced if the pH is uncontrolled, but effective mixing and pH control can limit their concentrations to satisfactory levels. pH is controlled by lime or caustic additions. This process required ≈ 8 mg Cl_2 per mg $\text{NH}_3\text{-N}$ and does significantly increase the total dissolved solids content of an effluent. This may in some cases limit the application of this process for the removal of the bulk of the ammonia from wastewater. Consideration should be given to use of breakpoint chlorination as a polishing operation where ammonia concentrations are low. Cost depends upon the required chlorine dosage.

One additional chemical approach has been an investigation of chemical denitrification using ferrous sulfate and a copper catalyst to convert nitrate ion to nitrogen gas. The reaction kinetics are not completely understood, pH must be controlled, and common interferences are phosphate and carbonate ions. A difficult to dewater ferrous-ferric hydroxide sludge is the product of the reaction.

The last entry on Table III represents the nitrogen removal step of the staged biological nitrification-denitrification process which will be discussed in detail today.

A very important observation is that all the nitrogen removal processes listed depend upon the nitrogen to be in a specific ionic form. For instance, if an acceptable ion-exchange process did become available, we would have to insure that nitrogen was in the proper ionic form for capture. Organic nitrogen compounds may be biologically converted to the proper ionic form but also are removed by coagulation and carbon adsorption.

A critical differentiation exists between treatment and control of nitrogen by the biological approach and the physical-chemical approach. Biological systems can be used to either produce a nitrified effluent or remove nitrogen by denitrification. All present physical-chemical processes operate as nitrogen removal processes.

Biological nitrification-denitrification is currently the most advanced technology for control of nitrogen.

A key feature of the biological nitrification-denitrification design is that the stage concept can allow initial construction to proceed through the first two stages for nitrification, and the third stage for denitrification need not be added until a nitrogen removal requirement is definitely established.

If the solution to an environmental problem would be nitrification, it would be economically undesirable to institute treatment for biological nitrogen removal.

If nitrogen removal is necessary, there are several alternate designs that can be considered. Figure 1 shows these variations. As of this date the suspended growth reactor would be favored in any large installation. This is mainly due to our familiarity with the design of the hydraulics in this type plant, our prior experience with these systems, and our large-scale demonstration results employing this type reactor.

Fine grain media in the range of 2-4 mm has so far been applied only to pilot scale, or very short-term demonstration studies. Uncertainties still exist about the frequency of backwash and the effects of backwash on the process and the media over an extended period of time. However, the hydraulic application rate of 7 gpm/ft² is very favorable and work is continuing on this type media. This approach could also offer the additional advantage of filtration in combination with the denitrification.

Large media, in the range of 0.5 to 1.0 inches, has been evaluated at Firebaugh, California, over a one-year period. Plugging of this column has occurred and re-design of the packing arrangement is necessary to insure that backwashing can reinstitute even hydraulic application. The flow rate to this column was 0.5 gpm/ft². This large media is similar to a trickling filter in that periodic sloughing of the growth occurs and a filtration step would be necessary to produce a high quality water.

The stage approach to nitrification is being applied at a number of sites either as demonstrations under EPA sponsorship or under active design by private consultants. Below are brief listings of these:

Hatfield Township, Pa. (5 mgd) - A solids contactor for phosphorus and organic removal, by use of lime, followed by a second stage suspended growth biological nitrification and multi-media filtration.

Stanford University, Calif. (Pilot-plant scale) - Second stage nitrification, using 1-inch media in flooded columns. Pure oxygen is being used.

Hobbs, New Mexico (5 mgd) - Nitrogen and phosphorus removal employing the three-sludge suspended growth reactors.

Manassas, Va. (0.2 mgd) - Nitrogen and phosphorus removal employing the three-sludge suspended growth reactors.

Midland, Mich. (Demonstration scale) - Second stage nitrification using attached growths on plastic media at 1 gpm/ft², direct tri-media filtration of tower effluent.

Washington, D.C. (300 mgd) - Nitrogen and phosphorus removal employing the three-sludge suspended growth reactors.

Tampa, Fla. (50 mgd) - Nitrogen and phosphorus removal employing the three-sludge suspended growth reactors. Other modifications under consideration.

Salt Creek, Ill. (50 mgd) - Two-stage nitrification with suspended growth reactors, third-stage denitrification on fine grain media; if required.

El Lago, Texas (0.5 mgd) - First-stage trickling filter, second-stage suspended growth nitrification, third-stage large media denitrification, effluent filtration, phosphorus removal in the primary tank.

Waukegan, Ill. (30 mgd) - Several plants totaling 30 mgd will be designed for two-stage nitrification employing suspended growth reactors.

Flint, Mich. (20 mgd) - Phosphorus and organic removal in primary tanks by metal salt and polymer. Nitrification in existing activated sludge tanks.

Fairfax County, Va. (Demonstration scale) - Phosphorus removal in primary tank with metal salt and polymer, second-stage suspended growth nitrification, third-stage denitrification in column packed with plastic rings. Effluent filtration.

TABLE I

IMPORTANCE OF NITROGEN

NH_3 IN EFFLUENTS CAN CAUSE DO SAG IN RECEIVING WATER

NH_3 IS CORROSIVE TO COPPER FITTINGS

1 NH_3 REQUIRES 7 PLUS Cl_2 FOR BREAKPOINT

NO_2 CAUSES HIGH Cl_2 DEMAND

NH_3 INFLUENCES Cl_2 CONTACT TIME

NITROGEN COMPOUNDS ARE NUTRIENTS

NO_3 CAN BE HEALTH HAZARD

NH_3 CAN BE TOXIC TO FISH

TABLE II

**RELATIONSHIP OF CARBONACEOUS OXIDATION AND AMMONIA OXIDATION,
BEFORE AND AFTER TREATMENT TO REMOVE 90% OF CARBONACEOUS
MATERIAL**

	mg/l	
	WASTE WATER	FINAL EFFLUENT
ORGANIC MATTER	250	25
ORGANIC OXYGEN DEMAND	375	37
NH ₃	25	20
AMMONIA OXYGEN DEMAND	112	90
TOTAL OXYGEN DEMAND	487	127
PERCENT OF OXYGEN DEMAND DUE TO NH ₃	22%	71%

TABLE III

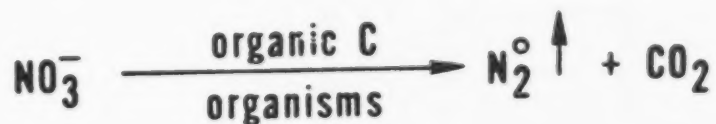
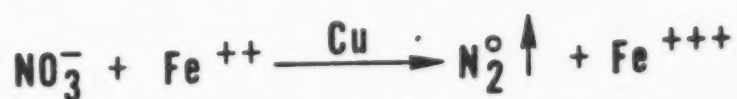
NITROGEN REMOVAL PROCESSES



REVERSE OSMOSIS

ELECTRODIALYSIS

DISTILLATION



MODIFICATIONS OF THE DENITRIFICATION PROCESS

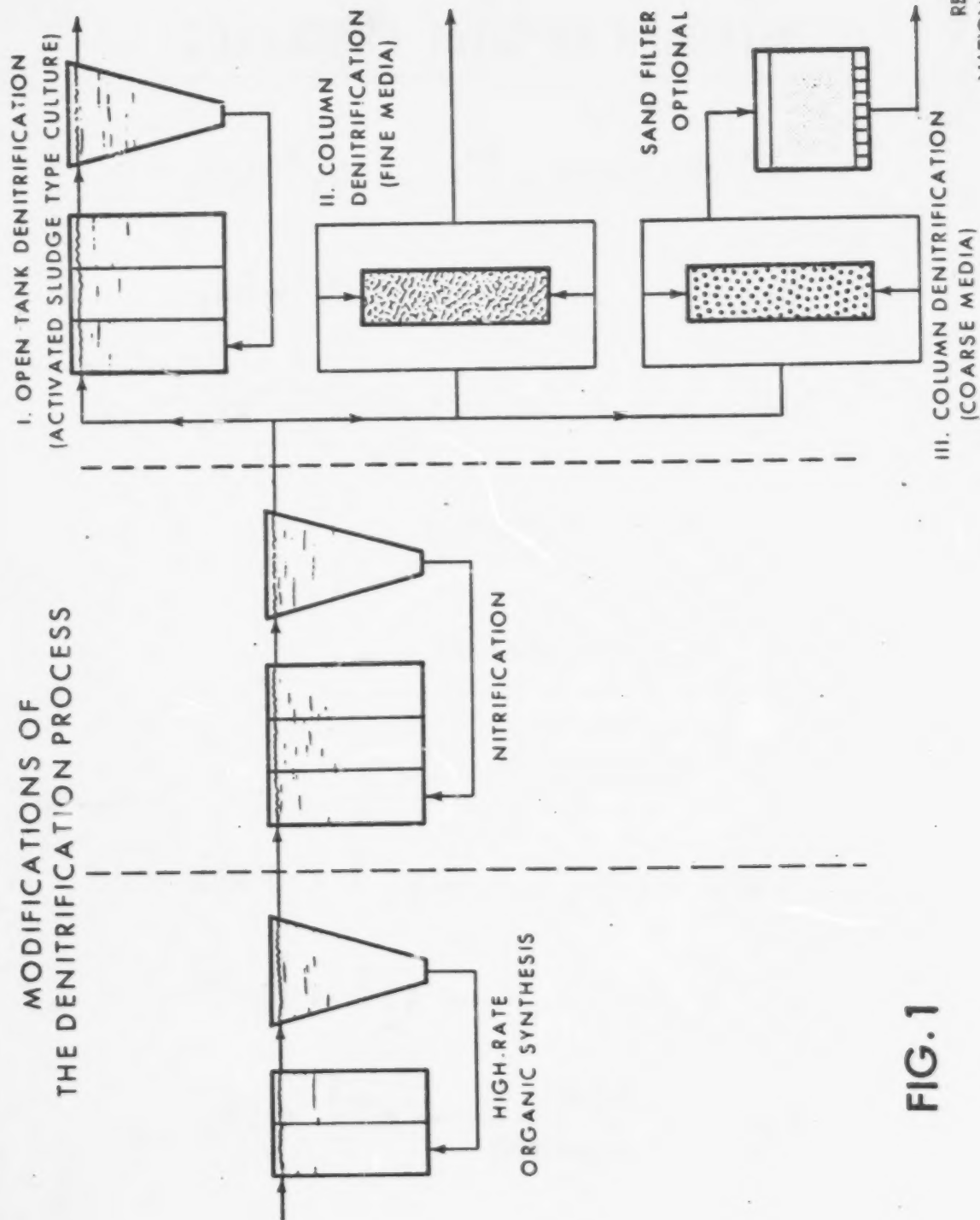


FIG. 1

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